Electronic structure of the chromium dioxide (001) surface

H. van Leuken and R. A. de Groot
Research Institute of Materials, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands
(Received 14 October 1994)

Local-density calculations on the CrO_2 (001) surface are reported. The half-metallic character of the bulk is found to be maintained at the surface. Surface states of oxygen p character at the top of the valence band for the semiconducting spin direction are discussed.

INTRODUCTION

The electronic structure of chromium dioxide has attracted much attention in the past years. Band-structure calculations[1] predicted CrO_2 to be a half-metallic ferromagnet, i.e., a system which is metallic for one spin direction while at the same time insulating for the opposite spin direction. Photoemission measurements showed the compound to be an insulator for both spin directions, however.[2] The compound conducts electricity, but so may a dirty semiconductor. Recent measurements of the reflectivity confirm the results of the band-structure calculations.[3] As is well known, photoemission is a much more surface-sensitive technique as compared with optical spectroscopy, so the apparent contradiction between these two experimental results revives the question[4] of whether the electronic structure of CrO_2 at the surface may be substantially different from that of the bulk.

This question is particularly relevant because of the possible applications of CrO_2 in a spin-polarized scanning tunneling microscope (SPSTM). Half-metallic magnets show electrical conductivity for charge carriers of one spin direction exclusively, so they are ideal materials to serve as tips in a SPSTM measurement.[5] In view of these applications, it is of supreme importance to have a detailed knowledge of the electronic structure of CrO_2 both in the bulk and at the surface. In this paper we report electronic-structure calculations on the (001) surface of CrO_2 using the localized spherical-wave method in the periodic slab geometry.

STRUCTURE

CrO_2 crystallizes in the rutile structure. This structure is described by space group 136 (D_{4h}^{14}) of the International Tables.[6] The tetragonal cell has an a axis of 4.421 Å and a c axis of 2.916 Å. Chromium occupies the $2a$ positions and oxygen the $4f$ positions with positional parameter 0.3053. The structure consists of octahedrally coordinated chromium atoms. Of the low-index surface planes the (001) plane has the stoichiometric composition and is hence unlikely to undergo reconstruction. Also a stoichiometric (110) plane exists if a bridging oxygen is included.[7] The calculations reported here involve a geometry of seven CrO_2 (001) layers, with periodic boundary conditions in the in-plane directions, separated by three vacuum layers. The charge in the central vacuum layer was smaller than 0.02 electron units, while the magnetic moment in the central CrO_2 slab differed by $0.02\mu_B$ from the integral bulk value 2. The symmetry of the slab is c-centered orthorhombic [space group 65 (D_{2h}^{19}) from the International Tables], with $a=b=6.252\,24$ Å and $c=14.58$ Å. Calculations using the atomic-sphere approximation on systems with lower symmetry and octahedrally coordinated atoms, like the rutile structure, require a careful analysis and sometimes the introduction of empty spheres in order to circumvent an unphysical large overlap of Wigner-Seitz spheres. Empty spheres were introduced at the Wyckoff positions $4g$ with positional parameter 0.3053 and the Wyckoff $4d$ positions (contrary to the $4c$ positions in earlier work[1]). The Wigner-Seitz radii employed were 2.1816, 2.0916, 1.5912, and 1.6612 Å for Cr, O, empty sphere ($4g$), and empty sphere ($4d$), respectively. This implies a unit cell of 14 atoms for the bulk and 70 atoms for the periodic slab geometry.

COMPUTATIONAL DETAILS

The calculations employed the localized spherical-wave (LSW) method.[8] Exchange and correlation were taken into account by the method described by von Barth and Hedin.[9] Scalar relativistic effects were included.[10] The basis set included $4s$, $4p$, and $3d$ functions for chromium, $2s$ and $2p$ functions for oxygen, and $1s$ and $2p$ functions for the empty spheres. For the Bessel expansion of the central Hankel functions on neighboring sites, one l value higher than the values given above were employed. In the LSW method the tedious calculation of structure constants is avoided by localizing the trial wave functions on a set of atoms within a prescribed sphere around the site of the wave function. The spheres contained about 39 atoms. The contributions of the Hankel functions centered on the atoms in these spheres to the wave function outside the sphere were expanded on the central site up to $l=19$. The coefficients of the first 100 spherical harmonics were equated analytically to zero, while the remaining degrees of freedom (between 38 and 68) were employed to minimize the contributions from $l=10$ through $l=19$ by means of a least-squares procedure. Partial densities of states were obtained by employing a linear tetrahedron method. The choice of Wigner-Seitz radii has been discussed in the section labeled Structure.

RESULTS AND DISCUSSION

The bulk density of states (DOS) is very similar as reported before.[1] At low energies (off the panel of Fig. 1) there are states of oxygen $2s$ character. At higher energies one finds states of primarily oxygen $2p$ character. For the majority-spin direction one finds the chromium d states directly above the oxygen levels, straddling the Fermi energy, while for the minority-spin direction these states are higher in energy because of the exchange interaction and are positioned above E_f. Figure 1 also compares the density of states of bulk CrO_2 with the DOS of the CrO_2 (001) surface layer and consecutive layers away from the surface, as well as the DOS of the first vacuum layer (the second vacuum layer shows a negligible amount of charge and is thus irrelevant). An immediate conclusion is that the half-metallic character is maintained up to the surface in the calculation. As a matter of fact, the overall topology of the curves in Fig. 1 is remarkably similar. The behavior of the magnetic moments per formula unit is interesting. The central layer in the slab geometry shows a moment of $2.021\mu_B$. The deviation from the perfect bulk value of $2\mu_B$ is a direct measure of the applicability of the slab approach. The value increases slightly in the next layer towards the surface to $2.025\mu_B$. The subsurface layer shows a strong reduction of the magnetic moment to $1.722\mu_B$, while the surface layer has an enhancement of the moment to $2.185\mu_B$. The first vacuum layer shows a moment of $0.055\mu_B$, parallel to the surface moment. The main differences in electronic structure between surface and bulk are found in the surface oxygen atoms. The DOS of the $2s$ electrons (off the panel of Fig. 1) of the surface oxygen atoms is well separated from the others and are 1 eV higher in energy. The level is much narrower and shows a simple double structure reflecting the bonding and antibonding character of the surface-oxygen states with themselves and a strong reduction of interaction with more bulklike oxygens. The reason for this behavior is the unfavorable Madelung energy of the surface oxygen atoms as compared with the bulk. Also, the behavior of the surface-oxygen states in the vicinity of the Fermi energy is quite distinct. Since these states form the top of the valence band for the semiconducting spin direction and thus are potentially important in tunneling experiments, we will examine them in somewhat more detail. The surface DOS shows a contribution above the top of the valence band for this spin direction, which is constant in energy, strongly suggesting a two-dimensional character of the states involved. The states responsible for this spectral weight are oxygen p_x and p_y states of the surface layer. The dispersion of these states along the Σ line $(\alpha,0,0)$ and the Δ line $(0,\alpha,0)$ directions is shown in Fig. 2. The symmetry labels are according to Ref. 11. There are four states split off from the valence band at Γ. The states of Γ_{4-} and Γ_{3+} symmetry consist of oxygen p_y and p_z states and do not show any dispersion whatsoever in the Σ direction and a strong dispersion in the Y direction. These states differ by the coupling between the oxygen p

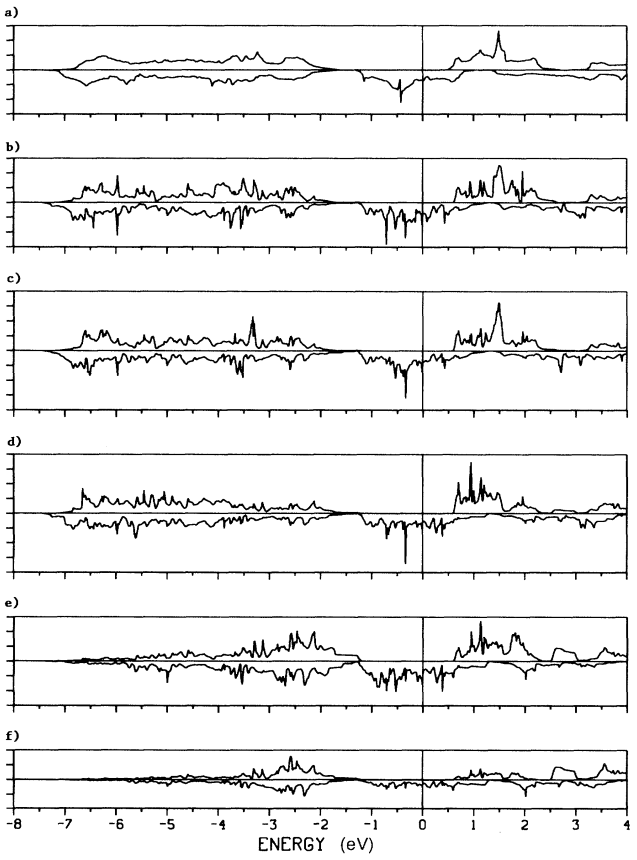

FIG. 1. Comparison of the density of states of bulk CrO_2 (a) with the density of states per layer of the CrO_2 (001) slab: central CrO_2 layer (b); sub-subsurface layer (c), subsurface layer (d), surface layer (e), and first vacuum layer (f). Vertical scale: 2 states per eV formula unit per division and 0.2 states per eV formula unit per division for (f).

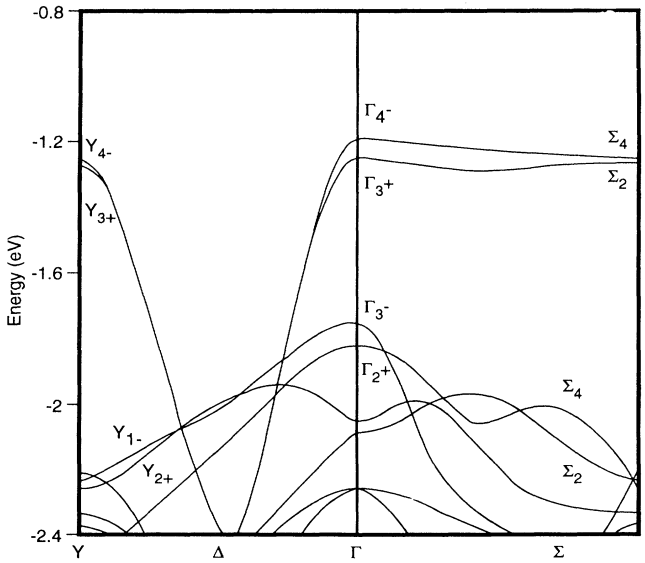

FIG. 2. Energy bands for the minority-spin direction at the top of the valence band along the two main directions of the two-dimensional Brillouin zone. Note the expanded vertical scale.

wave functions through the vacuum layers and the magnitude of the splitting (maximum 0.004 Ry at Γ) directly reflects the effect of the slab approximation. The states of symmetry Γ_{3-} and Γ_{2+} are oxygen p_x states, which show a modest dispersion in the Y direction and a stronger dispersion in the Σ direction leading to an overlap with bulk states. The dispersion found directly reflect the coordination of the surface oxygen atoms in the crystallographic x and y directions. The behavior at the bottom of the conduction band is very different from that of the top of the valence band: no states are split off in the gap and the character of the conduction band at the surface is very similar to bulk CrO_2.

ACKNOWLEDGMENTS

This research was sponsored by a Cray Research grant through the Stichting Nationale Computerfasciliteiten, the Technology Foundation (STW), and the Stichting voor Fundamenteel Onderzoek der Materie (FOM).

[1]K. Schwarz, J. Phys. F **16**, L211 (1986); S. Matar, G. Demazeau, J. Sticht, V. Eyert, and J. Kübler, J. Phys. (France) I **2**, 315 (1992).

[2]K. P. Kämper, W. Schmitt, G. Güntherodt, R. J. Gambino, and R. Ruf, Phys. Rev. Lett. **59**, 2788 (1987).

[3]H. Brändle, D. Weller, J. C. Scott, J. Sticht, P. M. Oppeneer, and G. Güntherodt, Int. J. Mod. Phys. **7**, 345 (1993).

[4]R. A. de Groot, Europhys. News **23**, 146 (1992).

[5]R. Wiesendanger, H.-J. Güntherodt, G. Güntherodt, R. J. Gambino, and R. Ruf, Phys. Rev. Lett. **65**, 247 (1990); Z. Phys. B **80**, 5 (1990).

[6]*International Tables for Crystallography,* edited by T. Hahn (Reidel, Dordrecht, 1983), Vol. A.

[7]For a clear picture of surface planes in the rutile structure, see D. Vogtenhuber, R. Podloucky, A. Neckel, S. G. Steinemann, and A. J. Freeman, Phys. Rev. B **49**, 2099 (1994).

[8]H. van Leuken, A. Lodder, M. T. Czyżyk, F. Springelkamp, and R. A. de Groot, Phys. Rev. B **41**, 5613 (1990).

[9]U. von Barth and L. Hedin, J. Phys. C **5**, 1629 (1972).

[10]M. Methfessel and J. Kübler, J. Phys. F **12**, 141 (1982).

[11]S. C. Miller and W. F. Love, *Tables of Irreducible Representations of Space Groups and Co-Representations of Magnetic Space Groups* (Pruett, Colorado, 1967).